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## Study of the Isothermal Bulk Copolymerization of Acrylic and Methacrylic Acid Esters\*

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### ABSTRACT

The course and kinetics of the isothermal bulk polymerization of ethyl acrylate, 2-ethylhexyl acrylate, and methyl methacrylate and their copolymerization in different mol ratios were studied by differential scanning calorimetry at 363 K. The initiator used was 2,2'-azoisobutyronitrile. The courses of reaction, the copolymerization enthalpies, the copolymerization parameters, and the specific constants of the rate of polymerization were determined.

### INTRODUCTION

The first to study the course and kinetics of the isothermal bulk polymerization of methyl methacrylate by differential scanning calorimetry (DSC) were Horie et al. [1]. The kinetics of polymerization of styrene by DSC was investigated by Ebdon et al. [2], and the copolymerization of styrene and acrylonitrile by Sebastian and

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\*Part of this work was presented at the IUPAC 28th Macromolecular Symposium in Amherst, Massachusetts, July 1982.

and Biesenberger [3]. Theoretically, the enthalpy of copolymerization was studied by Sawada [4] and Alfrey and Lewis [5].

By a similar method using DSC, we 1) studied the course and kinetics, under various conditions, of isothermal bulk polymerization of methyl methacrylate [6] and vinyl acetate [7]; and 2) compared the course of isothermal bulk polymerization of three acrylic monomers differing only in the substituent on the second C atom in the molecule: methyl acrylate, methyl methacrylate, and methyl-2-chloroacrylate in the presence or absence of  $ZnCl_2$  [8].

The kinetics of polymerization of esters of methacrylic acid, mainly of methyl methacrylate, at low and high conversion was studied extensively theoretically and practically also by other methods than DSC. It was found that the increased viscosity of the reaction medium causes a decrease of the mobility of polymer radicals and that therefore the termination is diffusion controlled [9-14].

Theoretically, the diffusion-controlled reaction can be divided into three processes: the translational diffusion of the center of mass of the polymer molecules; the translational and rotational diffusion of the active chain-ends (segmental diffusion); and, after all positional factors are favorable, the chemical reaction. At the radical termination reactions of alkyl methacrylates, the segmental diffusion process of the chain ends is the rate-determining step [11, 13].

The polymerization of esters of acrylic acid was also investigated. It was found that the rate of polymerization is higher than the rate of polymerization of esters of methacrylic acid and that the rate is affected by ester groups due to steric effects [15-17].

In the present work the enthalpy of the radical bulk copolymerization of ethyl acrylate (EA) with 2-ethylhexyl acrylate (EHA) and of methyl methacrylate (MMA) with EA and EHA was measured by DSC during the entire reaction time.

## EXPERIMENTAL

### Materials

EA, MMA, and EHA were freed of inhibitor and distilled under nitrogen at reduced pressure. The initiator 2,2'-azoisobutyronitrile (AIBN) was recrystallized from absolute ethanol.

### Method

The radical copolymerization of EA with EHA, EA with MMA, and EHA with MMA in molar ratios 3:1, 1:1, and 1:3 was investigated isothermally at 363 K using the differential scanning calorimeter DSC-2, Perkin-Elmer. To have a suitable time of polymerization

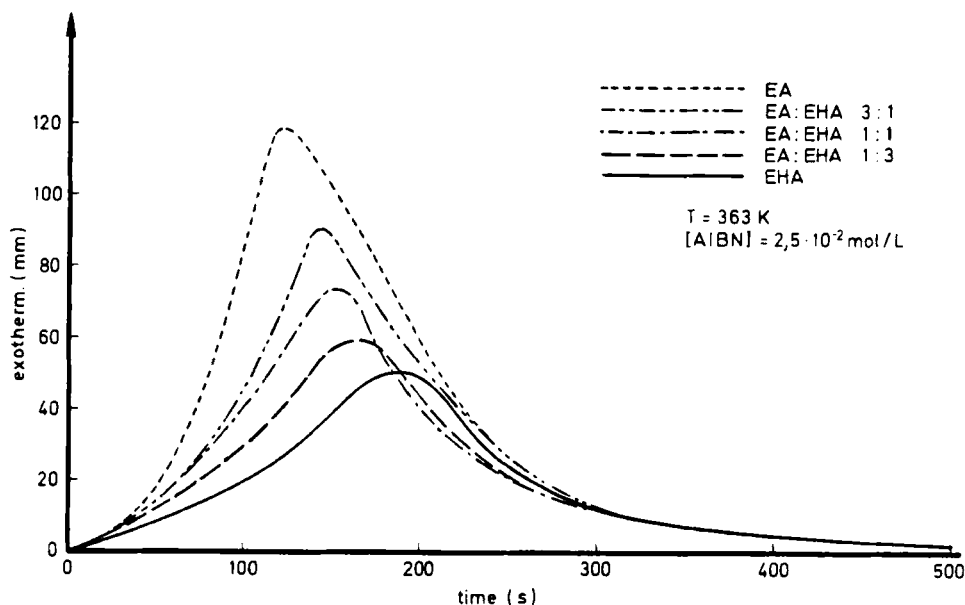


FIG. 1. Course of isothermal polymerization of EA and EHA and their copolymerization in molar ratios 3:1, 1:1, and 1:3 at 363 K in the presence of  $2,5 \times 10^{-2}$  mol/L AIBN.

for measurements in DSC,  $2,5 \times 10^{-2}$  mol/L of AIBN was added as initiator in the case of polymerization of EA with EHA and  $5 \times 10^{-2}$  mol/L in the case of EA with MMA and EHA with MMA. The enthalpy of copolymerization was calculated from the areas between the DSC curves and the baseline [6] which was obtained by back-extrapolation of the straight line, recorded after the polymerization was finished.

The calorimeter was calibrated with reference to the melting heat of indium. The DSC curves were digitized on-line and processed by the computer.

## RESULTS AND DISCUSSION

Figure 1 shows the course of the isothermal bulk homopolymerization of EA and EHA and the course of copolymerization of EA with EHA. Under the same conditions the polymerization of EA is faster and more exotherm than the polymerization of EHA. The polymerization of EA and EHA and their copolymerization is very fast immediately after the beginning of the reaction, similar to the polymerization of methyl acrylate [8]. For this reason the usual method

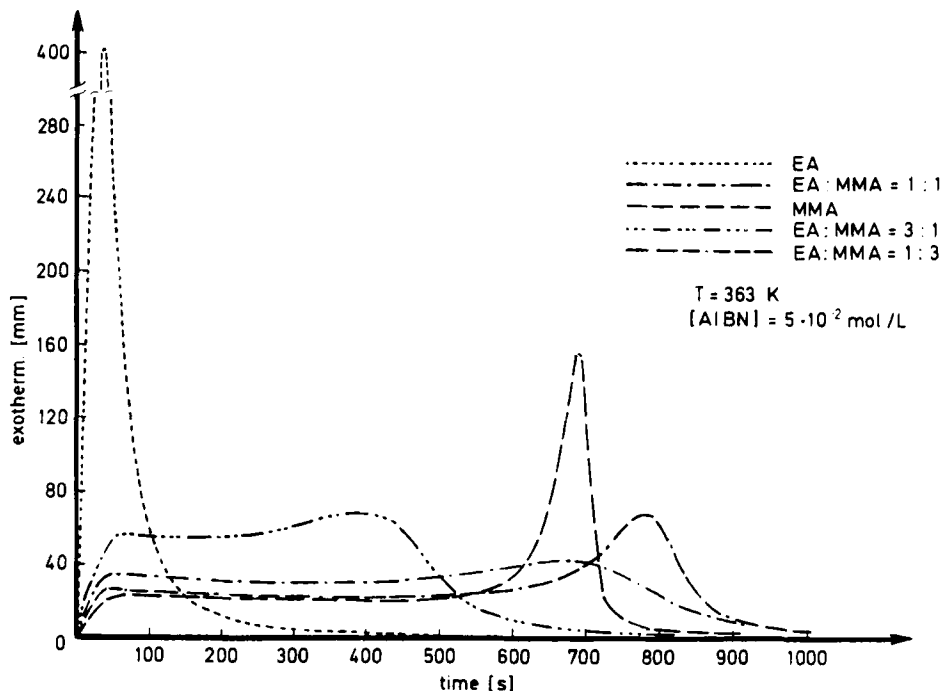


FIG. 2. Course of isothermal polymerization of EA and MMA and their copolymerization in molar ratios 3:1, 1:1, and 1:3 at 363 K in the presence of  $5 \times 10^{-2}$  mol/L AIBN.

for evaluation of kinetics at steady-state conditions as in the case of MMA [6] could not be used.

From these data and from published results it can be concluded that the polymerization of all acrylic esters proceeds in a similar way, differing only in the rate of polymerization. However, substitution of the second C atom in the molecule of acrylic acid esters, which influences the mobility of the polymer chain and increases steric hindrance during polymerization, can change the course of polymerization.

Therefore, for further work MMA was chosen as comonomer. Figure 2 shows the course of polymerization of MMA and EA and the course of copolymerization of MMA with EA, and Fig. 3 shows the corresponding courses for MMA and EHA. As expected, in the initial part of reaction the rate of reaction is nearly constant in all systems. The steady-state part of the reaction is of different duration for different systems.

For instance, in the copolymerization of MMA with EHA in

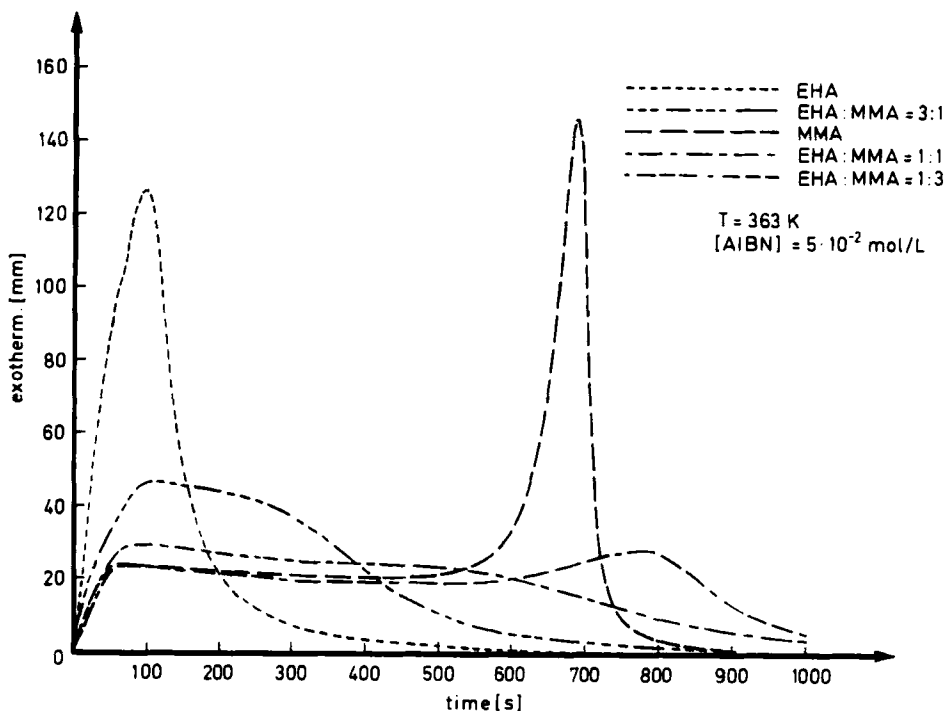


FIG. 3. Course of isothermal polymerization of EHA and MMA and their copolymerization in molar ratios 3:1, 1:1, and 1:3 at 363 K in the presence of  $5 \times 10^{-2}$  mol/L AIBN.

equimolar ratio, the accelerated reaction characteristic for each monomer completely disappeared.

The course of polymerization of MMA measured by DSC is in agreement with the model predicted by Dionisio and O'Driscoll [18] for polymerization at high conversion, expressed by the following equations:

$$\frac{dx}{dt} = k_p \left( \frac{fk_d}{k_t} \right)^{1/2} [I]^{1/2} (1-x)(1+\gamma) \quad (1)$$

where  $x$  is conversion of monomer

$t$  is the time

$k_d$ ,  $k_p$ ,  $k_t$  are rate constants for initiator decomposition, polymerization, and termination between non-entangled radicals

$f$  is the initiator efficiency  
 $[I]$  is the initiator concentration  
 $\gamma$  is the gel effect index

and

$$\gamma = \left( \frac{1}{\alpha} - 1 \right) \exp \left( \frac{n_c}{\nu} \right) \quad (2)$$

where  $\alpha$  is a dimensionless parameter defined as  $(k_{tc}/k_t)^{1/2}$

$k_{tc}$  is the rate constant for the termination reaction between entangled radicals  
 $n_c$  is the critical polymer chain length  
 $\nu$  is the instantaneous chain length of the polymer produced from nonentangled radicals

The model proposes a critical chain length  $n_c$  such that the radicals with chains longer than  $n_c$  are considered to be entangled and therefore hindered from moving. After about 35% conversion, according to the proposed model, "most of the polymer chains are entangled and the nonentangled radicals terminate predominantly with the far more numerous entangled radicals," which is expressed as a sharp increase in the rate of release of polymerization enthalpy in the DSC curve. The "critical conversion" is temperature independent [6]. In the steady-state region of polymerization the last term of Eq. (1) is 1. Therefore Eq. (1) becomes the same as Eq. (5) that we normally use to evaluate the overall kinetic rate constant for polymerization from DSC data [6].

The molecular weight of the acrylic acid ester polymers is assumed to be in agreement with data found for MA. Namely, at the beginning of the reaction the degree of polymerization of MA was already found to be more than two times higher than the degree of polymerization of MMA [16]. Also, from sharp increase of the rate of reaction which can be seen in the DSC curves, it can be concluded that entanglement of the polymer chains starts immediately. The fact that the gel effect is less expressed in copolymers can be explained only with changed conditions when a comonomer is being incorporated into the polymer chain. The incorporation may change the flexibility of polymer chains, alter the dimensions of the coiled polymer chains [19], and affect steric hindrances.

The copolymerization enthalpies calculated from the areas under the DSC curves are given in Table 1 and Fig. 4.

Sawada [4] proposed for random copolymerization

$$\Delta H_{\text{cop}} = \Delta H_{11} X_1 + \Delta H_{22} X_2 + X_1 X_2 \Omega \quad (3)$$

TABLE 1. Copolymerization Enthalpies of EA with EHA, EA with MMA, and EHA with MMA at 363 K,  $[AIBN] = 2.5 \times 10^{-2}$  mol/L\* or  $5 \times 10^{-2}$  mol/L\*\*

Sample	Copolymerization enthalpies (kJ/mol)					$\Omega$
	Monomer 1	3:1	1:1	1:3	Monomer 2	
EA-EHA*	80.7	80.0	79.4	78.8	78.2	-0.2
EA-MMA**	80.7	76.5	71.9	66.0	56.8	13.1
EHA-MMA**	78.2	74.4	69.8	63.5	56.8	8.2

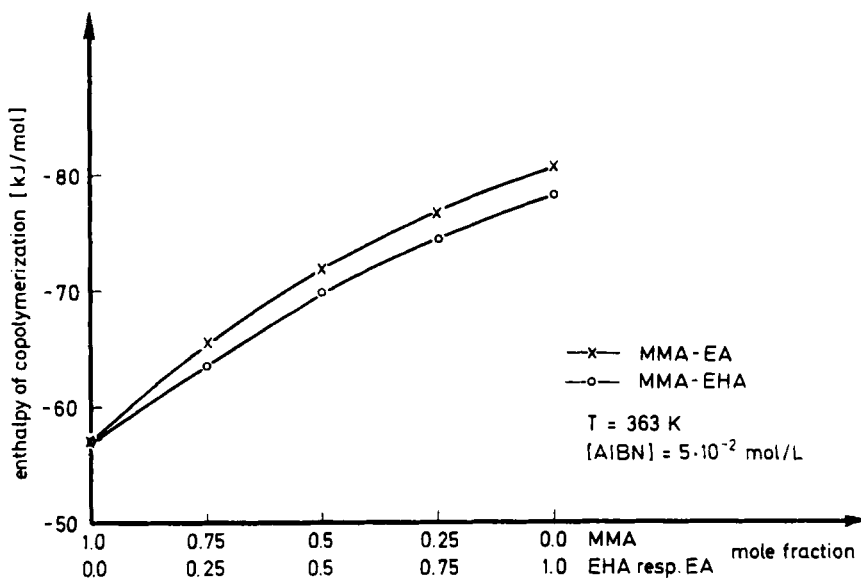


FIG. 4. Copolymerization enthalpies calculated from DSC data for the systems EA-MMA and EHA-MMA.

where  $\Delta H_{\text{cop}}$  is the copolymerization enthalpy,  $\Delta H_{11}$  and  $\Delta H_{22}$  are the polymerization enthalpies of Monomers 1 and 2,  $\Delta H_{12}$  and  $\Delta H_{21}$  are the copolymerization enthalpies of Monomer 1 with Monomer 2 and vice versa, and  $X_1$  and  $X_2$  are mol fractions of monomeric groups 1 and 2 in the copolymer.



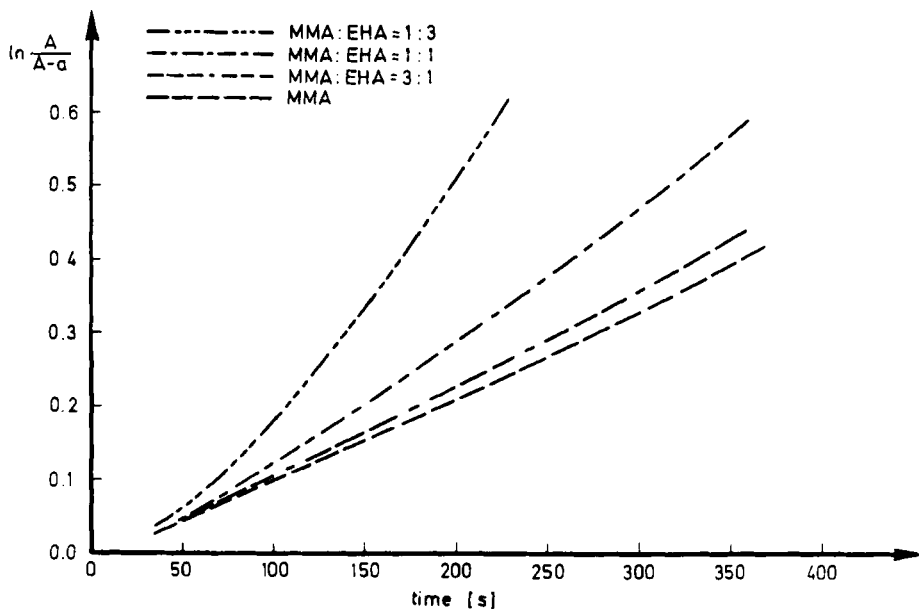


FIG. 5. Initial rate constants for the copolymerization of EHA with MMA in molar ratios 3:1, 1:1, and 1:3 at 363 K in the presence of  $5 \times 10^{-2}$  mol/L AIBN.

The copolymerization parameter  $\Omega$  is defined as

$$\Omega = \Delta H_{12} + \Delta H_{21} - (\Delta H_{11} + \Delta H_{22}) \quad (4)$$

and is independent of composition.  $\Omega$  for the copolymerization of EA with EHA, of EA with MMA, and of EHA with MMA was calculated. The values are given in Table 1.

By determining the areas under the DSC curves [6] by using the equation

$$\ln \left( \frac{A}{A-a} \right) = k't \quad (5)$$

where  $k'$  is the composite rate constant  $k_p \left( \frac{fk_d}{k_t} \right)^{1/2} [I_0]^{1/2}$ ,  $A$  is

the total area, and  $a$  is the partial area under the DSC curve up to time  $t$ , the overall rate constants of copolymerization within the

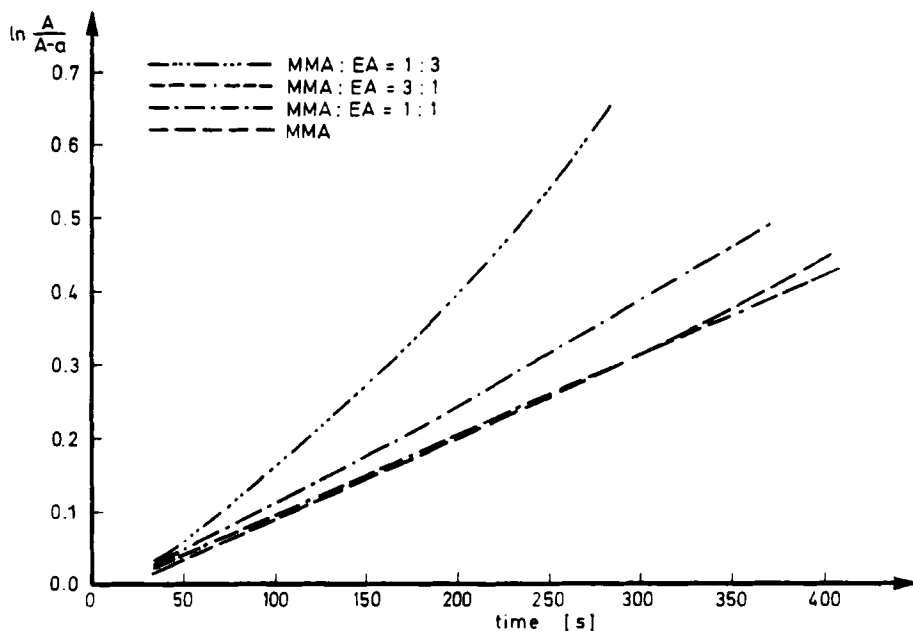


FIG. 6. Initial rate constants for the copolymerization of EA with MMA in molar ratios 3:1, 1:1, and 1:3 at 363 K in the presence of  $5 \times 10^{-2}$  mol/L AIBN.

TABLE 2. Composite Rate Constants of Copolymerization for the System MMA-EHA and MMA-EA,  $T = 363$  K,  $[AIBN] = 5 \times 10^{-2}$  mol/L

Sample	$k' (s^{-1}) \times 10^3$
MMA	1.1
MMA-EHA 3:1	1.2
MMA-EHA 1:1	1.6
MMA-EHA 1:3	1.8
MMA-EA 3:1	1.1
MMA-EA 1:1	1.3
MMA-EA 1:3	2.1

steady-state of reaction for the first-order reaction with respect to the monomer concentration were evaluated. The areas and rate constants were calculated by on-line digitizing the DSC curves and processing them by computer. Figure 5 shows the plot of

$\ln \left( \frac{A}{A-a} \right)$  vs time for the copolymerization of MMA with EHA and

Fig. 6 for the copolymerization of MMA with EA. The composite rate constants were calculated from the linear part of the curves. The values obtained are given in Table 2. The linear parts of these diagrams becomes shorter with an increase of acrylic acid ester concentrations.

### CONCLUSIONS

The polymerization of acrylic acid esters proceeds very fast at the beginning of the reaction, while the polymerization of methacrylic acid esters is stationary in the early stage of polymerization, obeying the first-order reaction with respect to the monomer concentration. This stage is followed by a strongly expressed gel effect. In copolymerizations the initial rate of polymerization of acrylic acid esters and the gel effect of methacrylic acid esters are moderated. At some ratios between the monomers the accelerated reaction completely disappears. From DSC curves of the enthalpies of copolymerization, the composite rate constants for the first-order reaction were calculated, while from enthalpy vs copolymer composition diagrams the copolymerization parameters  $\Omega$  were calculated.

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